

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

Kazuyuki HAYASHI et al

SERIAL NO. 09/940,866

GROUP ART UNIT: 1714

FILED: August 29, 2001

EXAMINER: Katarzyna

Wyrozebski

FOR: COMPOSITE PARTICLES, PROCESS  
FOR PRODUCING THE SAME, AND  
PIGMENT, PAINT AND RESIN  
COMPOSITION USING THE SAME

DECLARATION UNDER 37 C.F.R. 1.132

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WASHINGTON, D.C. 20231

SIR:

Now comes Kazuyuki HAYASHI, a citizen of Japan, and a resident of 34-43-20, Kawauchi 6-chome, Asaminami-ku, Hiroshima-shi, Hiroshima-ken, Japan, who declares and says that:

1. I graduated from Faculty of Engineering, Osaka Prefecture University in March, 1982; received a master's degree from the graduate school of the same university in March 1984.

2. I am currently employed by TODA KOGYO CORPORATION since 1984.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 09/940,866, and am a co-inventor of the U.S. Patents: No. 6,287,668, No. 6,294,242, No.



6,352,776, No. 6,416,864, No. 6,458,453, 6,531,211, and No. 6,544,647.

4. I have read the Office Action dated August 22, 2002, have understand the Examiner's rejection to the invention claimed in the above application, and have ascertained the following.

Experiment 1 (Example I of U.S. Patent No. 5,378,574)

To 9.6 g of Aerosil® 200, which had been dried at 100°C for 24 hours in a 500 ml round bottom flask equipped with a magnetic stirrer and a Dean-Stark trap, were added 300 ml of toluene, which had previously been dried by azeotropic distillation under nitrogen, and 2.96 g of aminopropyltriethoxysilane. The resulting suspension was refluxed at 111°C for 5 hours, cooled to room temperature, and centrifuged at about 10,000 r.p.m., after which the supernatant liquid was poured off and the precipitate washed with 500 ml of dichloromethane. Subsequently, the mixture of precipitate and dichloromethane was centrifuged, the supernatant was removed, and the residue was dried in a vacuum oven at about 200 mm Hg at 40°C for 2.5 days to yield 9.6 g (76% yield) of a white powdery material comprising Aerosil® 200 particles having covalently attached thereto aminopropyltriethoxysilane groups.

Experiment 2 (Example VII of U.S. Patent No. 5,378,574)

A mixture of 1.0 g of silica particles with attached couplers prepared in Experiment 1 and 1.0 g of Levafix Brilliant Blue EFFA (available from Bayer) in 40 ml of water was stirred at room temperature for 18 hours in a round bottom flask equipped with a magnetic stirrer and was subsequently centrifuged. The residue was dispersed in water and centrifuged in water until the supernatant was colorless, after which the residue was redispersed in water and freeze-dried with a Small-sized Freeze Dryer (DFR-5N-A, manufactured by ULVAC Co., Ltd.) (Note: Since "Dura-Dry® freeze dryer" manufactured by FTS.RTM. Systems, Stone Ridge, N.Y., had not been available promptly, the Small-sized Freeze Dryer (DFR-5N-A) was used instead of "Dura-Dry® freeze dryer".), to yield 0.75 g of blue silica particles as composite particles.

The properties in the particles were measured by the following methods.

(1) The average particle size of the particles was expressed by an average value of 350 particles observed on a micrograph.

(2) The specific surface area was expressed by the value measured by a BET method.

(3) The hue of blue silica particles, coating film and resin composition was measured by the following method.

That is, 0.5 g of sample and 0.5 ml of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied on a cast-coated paper by using a 150  $\mu\text{m}$  (6-mil) applicator to produce a coating film piece (having a film thickness of about 30  $\mu\text{m}$ ). The thus obtained coating film piece was measured by a multi-spectro-colour-meter "MSC-IS-2D" (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine L\*, a\* and b\* values thereof, respectively.

(4) The tinting strength of the blue silica particles was measured by the following method.

That is, a primary color enamel and a vehicle enamel prepared by the below-mentioned method were respectively applied on a cast-coated paper by a 150  $\mu\text{m}$  (6-mil) applicator to produce coating film pieces. The thus obtained coating film pieces were measured by a multi-spectro-colour-meter "MSC-IS-2D" (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine L\* values thereof. The difference between the obtained L\* values was represented by a  $\Delta\text{L}^*$  value.

Next, as a standard sample for the blue silica particles, a mixed dye was prepared by simply mixing the dye and the silica particles at the same mixing ratio as

used for the production of the blue silica particles. Using the thus prepared mixed pigment as standard sample, the same procedure as defined above was conducted to prepare an primary color enamel and a vehicle enamel, form coating film pieces and measure L\* values thereof. The difference between the L\* values was represented by a  $\Delta Ls^*$  value.

From the obtained  $\Delta L^*$  value of the blue silica particles and  $\Delta Ls^*$  value of the standard sample, the tinting strength (%) was calculated according to the following formula:

$$\text{Tinting strength (\%)} = 100 + \{(\Delta Ls^* - \Delta L^*) \times 10\}$$

Preparation of primary color enamel:

10 g of the above blue silica particles, 16 g of an amino alkyd resin and 6 g of a thinner were blended together. The resultant mixture was added together with 90 g of 3mmΦ glass beads into a 140-ml glass bottle, and then mixed and dispersed for 45 minutes by a paint shaker. The obtained mixture was mixed with 50 g of an amino alkyd resin, and further dispersed for 5 minutes by a paint shaker, thereby obtaining an primary color enamel.

Preparation of vehicle enamel:

12 g of the above-prepared primary color enamel and 40 g of Aramic White (titanium dioxide-dispersed amino alkyd resin) were blended together, and the resultant mixture was mixed and dispersed for 15 minutes by a paint shaker,

thereby preparing a vehicle enamel.

(5) The hiding power of the blue silica particles was measured by the cryptometer method according to JIS K5101-8.2 using the above-prepared primary color enamel.

(6) The light resistance of the blue silica particles was measured by the following method.

That is, the same primary color enamel as prepared above for the measurement of tinting strength, was applied onto a cold-rolled steel plate (0.8 mm × 70 mm × 150 mm; JIS G-3141) and dried to form a coating film having a thickness of 150 µm. One half of the thus prepared test specimen was covered with a metal foil, and an ultraviolet light was continuously irradiated over the test specimen at an intensity of 100 mW/cm<sup>2</sup> for 6 hours using "EYE SUPER UV TESTER SUV-W13" (manufactured by IWASAKI DENKI CO., LTD.). Then, the hues (L\*, a\* and b\* values) of the metal foil-covered non-irradiated portion and the UV-irradiated portion of the test specimen were respectively measured. The ΔE\* value was calculated from differences between the measured hue values of the metal foil-covered non-irradiated portion and the UV-irradiated portion according to the following formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

wherein ΔL\* represents the difference between L\* values of

the non-irradiated and UV-irradiated portions;  $\Delta a^*$  represents the difference between  $a^*$  values of the non-irradiated and UV-irradiated portions; and  $\Delta b^*$  represents the difference between  $b^*$  values of the non-irradiated and UV-irradiated portions.

(7) The hues of the solvent-based paint and water-based paint using the blue silica particles were measured by the following method.

That is, the respective paints prepared by the below-mentioned methods, were applied onto a cold-rolled steel plate (0.8 mm × 70 mm × 150 mm; JIS G-3141) and dried to form a coating film having a thickness of 150  $\mu\text{m}$ . The thus obtained test specimens were measured by a multi-spectro-colour-meter "MSC-IS-2D" (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine  $L^*$ ,  $a^*$  and  $b^*$  values thereof.

<Production of solvent-based paint containing blue silica particles>

10 g of the blue silica particles produced in Experiment 2, were blended with an amino alkyd resin and a thinner at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mmΦ glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:

Blue silica particles	12.2 parts by weight
Amino alkyd resin (AMILAC No.	
1026, produced by KANSAI	
PAINT CO., LTD.)	19.5 parts by weight
Thinner	7.3 parts by weight

The above-prepared mill base was blended with an amino alkyd resin at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a solvent-based paint containing the blue silica particles.

Composition of paint:

Mill base	39.0 parts by weight
Amino alkyd resin (AMILAC	
No. 1026, produced by KANSAI	
PAINT CO., LTD.)	61.0 parts by weight

<Production of water-based paint containing blue silica particles>

7.62 g of the blue silica particles obtained in Experiment 2, were blended with a water-soluble alkyd resin and the like at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mmφ glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby

preparing a mill base.

Composition of Mill Base:

Blue silica particles 12.4 parts by weight

Water-soluble alkyd resin

(tradename: "S-118", produced

by DAI-NIPPON INK KAGAKU

KOGYO CO., LTD.)

9.0 parts by weight

Defoamer (tradename:

"NOPCO 8034", produced

by SUN NOPCO CO., LTD.)

0.1 part by weight

Water

4.8 parts by weight

Butyl cellosolve

4.1 parts by weight

The above-prepared mill base was blended with paint components shown below at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a water-based paint.

Composition of paint:

Mill base 30.4 parts by weight

Water-soluble alkyd resin

(tradename: S-118, produced

by DAI-NIPPON INK KAGAKU

KOGYO CO., LTD.)

46.2 parts by weight

Water-soluble melamine resin

(tradename: S-695, produced

by DAI-NIPPON INK KAGAKU  
KOGYO CO., LTD.) 12.6 parts by weight

Defoamer (tradename:  
"NOPCO 8034", produced  
by SUN NOPCO CO., LTD.) 0.1 part by weight

Water 9.1 parts by weight

Butyl cellosolve 1.6 parts by weight

(8) The hue of the resin composition was measured by the following method.

That is, a colored resin plate prepared by the below-mentioned method was measured by a multi-spectro-colour-meter "MSC-IS-2D" (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) by the same method as described above.

<Production of resin composition>

2.5 g of the blue silica particles obtained in Experiment 2, and 47. 5 g of polyvinyl chloride resin particles 103EP8D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100-ml beaker made of resins, and intimately mixed together by a spatula, thereby obtaining mixed particles.

0.5 g of calcium stearate was added to the obtained mixed particles. The mixed particles were intimately mixed and then slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded

therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and then subjected to a pressure molding while applying a pressure of 98MPa (1 ton/cm<sup>2</sup>) thereto, thereby obtaining a colored resin plate having a thickness of 1 mm.

(9) The gloss of the coating film obtained for determining the hue, was measured by irradiating light at an incident angle of 60°, using a gloss meter UGV-5D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.). The higher the gloss, the more excellent the dispersibility of the blue silica particles in the paint.

(10) The light resistance of coating films produced from the paint, was measured by the following method.

That is, one half of the same test specimen as prepared and used for measuring hues of the above paints, was covered with a metal foil, and an ultraviolet light was continuously irradiated over the test specimen at an intensity of 100 mW/cm<sup>2</sup> for 6 hours using "EYE SUPER UV TESTER SUV-W13" (manufactured by IWASAKI DENKI CO., LTD.).

Then, the hues ( $L^*$ ,  $a^*$  and  $b^*$  values) of the metal foil-covered non-irradiated portion and the UV-irradiated portion of the test specimen were respectively measured. The  $\Delta E^*$  value was calculated from differences between the measured hue values of the metal foil-covered non-irradiated portion and the UV-irradiated portion according to the above-described formula.

(11) The light resistance of the resin composition, was measured by the following method.

That is, one half of the same resin plate as prepared and used for measuring hues of the above resin composition, was covered with a metal foil, and an ultraviolet light was continuously irradiated over the resin plate at an intensity of  $100 \text{ mW/cm}^2$  for 6 hours using "EYE SUPER UV TESTER SUV-W13" (manufactured by IWASAKI DENKI CO., LTD.). Then, the hues ( $L^*$ ,  $a^*$  and  $b^*$  values) of the metal foil-covered non-irradiated portion and the UV-irradiated portion of the resin plate were respectively measured. The  $\Delta E^*$  value was calculated from differences between the measured hue values of the metal foil-covered non-irradiated portion and the UV-irradiated portion according to the above-described formula.

(12) The transparency of the coating film using the blue silica particles was expressed by the linear

absorption defined by the following formula. Specifically, the linear absorption was calculated from the light transmittance of a coating film produced by applying a paint prepared by the below-mentioned method on a 100 $\mu\text{m}$ -thick clear base film. The light transmittance was measured using a self-recording photoelectric spectrophotometer "UV-2100" (manufactured by SHIMADZU SEISAKUSHO CO., LTD.).

Also, the transparency of the resin composition was expressed by the linear absorption of a resin plate having the following composition. The linear absorption was calculated from the light transmittance of the resin plate which was measured using a self-recording photoelectric spectrophotometer "UV-2100" (manufactured by Shimadzu Seisakusho CO., LTD.). The smaller the linear absorption, the higher the light transmittance and the higher the transparency.

$$\text{Linear absorption } (\mu\text{m}^{-1}) = \ln(1/t)/FT$$

wherein t is a light transmittance (-) at  $\lambda = 900$  nm; FT is a thickness ( $\mu\text{m}$ ) of the coating film or resin plate to be tested.

Preparation of paint for evaluation of transparency:

5 g of blue silica particles and the other components shown below were added at the following weight ratio into a 250-ml glass bottle, and then mixed and dispersed therein

together with 160 g of 3mmØ glass beads for 120 minutes by a paint shaker, thereby preparing a paint for evaluation of transparency.

Composition of paint for evaluation of transparency:

Sample particles	9.9 parts by weight
Melamine resin (SUPER PECKAMINE	
J-820-60 (tradename) produced by	
DAI-NIPPON INK KAGAKU KOGYO	
CO., LTD.)	19.8 parts by weight
Alkyd resin (BECKOZOL 1307-60EL	
(tradename) produced by DAI-NIPPON	
INK KAGAKU KOGYO CO., LTD.)	39.6 parts by weight
Xylene	29.7 parts by weight
Butanol	1.0 part by weight

Preparation of water-based paint for evaluation of transparency:

5 g of blue silica particles and the other components shown below were added at the following weight ratio into a 250-ml glass bottle, and then mixed and dispersed therein together with 160 g of 3mmØ glass beads for 120 minutes by a paint shaker, thereby preparing a paint for evaluation of transparency.

Composition of water-based paint for evaluation of transparency:

Blue silica particles	10.1 parts by weight
Water-based melamine resin (S-695 (tradename) produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	9.3 parts by weight
Water-based alkyd resin (S-118 (tradename) produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	40.7 parts by weight
Defoamer (NOPCO 8034 (tradename) produced by SUN NOPCO CO., LTD.)	0.2 part by weight
Water	28.2 parts by weight
Butyl cellosolve	11.5 parts by weight

Preparation of resin composition for evaluation of  
transparency:

0.5 g of blue silica particles and 49. 5 g of polyvinyl chloride resin particles ("103EP8D" (tradename), produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker made of a resin, and intimately mixed together by a spatula, thereby obtaining mixed particles.

1.0 g of calcium stearate was added to the obtained mixed particles. The mixed particles were intimately mixed and then slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot

rolls and used as a raw material for forming a colored resin plate. Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and then subjected to a pressure molding while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto, thereby obtaining a colored resin plate for evaluation of transparency, having a thickness of 1 mm.

(13) The storage stability of the paint was measured by the following method.

That is, the respective paints obtained for determining the hue, were applied onto a cold-rolled steel plate (0.8 mm × 70 mm × 150 mm; JIS G-3141) and dried to form a coating film having a thickness of 150 µm. Then, the L\*, a\* and b\* values of the thus prepared coating film were measured. Separately, the respective paints were allowed to stand at 25°C for one week, and then applied onto the cold-rolled steel plate and dried to form a similar coating film. The L\*, a\* and b\* values of the thus prepared coating film were also measured. The ΔE\* value was calculated from the differences between the measured values according to the following formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

wherein ΔL\* represents the difference between L\* values

before and after the standing test;  $\Delta a^*$  represents the difference between  $a^*$  values before and after the standing test; and  $\Delta b^*$  represents the difference between  $b^*$  values before and after the standing test.

(14) The viscosity at 25°C of the paint obtained for determining the hue, was measured at a shear rate (D) of  $1.92 \text{ sec}^{-1}$  using an E-type viscometer (cone plate-type viscometer) EMD-R (manufactured by TOKYO KEIKI CO., LTD.).

(15) The dispersibility of the blue silica particles in the resin composition was evaluated by visually counting the number of undispersed aggregate particles on a surface of the obtained resin plate, and classifying the results into the following five ranks. The rank 5 represents the most excellent dispersing condition.

Rank 5: No undispersed aggregate particles were recognized.

Rank 4: 1 to 4 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 3: 5 to 9 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 2: 10 to 49 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 1: Not less than 50 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized.

The results are shown in the Tables 1 to 4.

Table 1

	Properties of blue silica particles	
	Average particle size ( $\mu\text{m}$ )	BET specific surface area value ( $\text{m}^2/\text{g}$ )
Our invention	0.001-10.0	1.0-500
Experiment 2	0.013	184

Table 1 (continued)

	Properties of blue silica particles		
	Hue		
	L* value (-)	a* value (-)	b* value (-)
Our invention	-	-	-
Experiment 2	34.86	8.0	-14.15

Table 1 (continued)

	Properties of blue silica particles		
	Tinting strength (%)	Hiding power ( $\text{cm}^2/\text{g}$ )	Light resistance ( $\Delta E^*$ value) (-)
Our invention	Not less than 110	Less than 700	Not more than 5.0
Experiment 2	108	560	12.1

Table 2

	Properties of solvent-based paint	
	Viscosity (cP)	Storage stability ( $\Delta E^*$ value) (-)
Our invention	-	Not more than 1.5
Experiment 2	1860	2.13

Table 2 (continued)

	Properties of coating film			
	60° gloss (%)	Hue		
		L* value (-)	a* value (-)	b* value (-)
Our invention	75-110	-	-	-
Experiment 2	72	34.91	8.38	-13.96

Table 2 (continued)

	Properties of coating film	
	Light resistance ( $\Delta E^*$ value) (-)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Our invention	Not more than 5.0	Not more than 0.10
Experiment 2	13.3	0.1065

Table 3

	Properties of water-based paint	
	Viscosity (cP)	Storage stability ( $\Delta E^*$ value) (-)
Our invention	-	Not more than 1.5
Experiment 2	2683	1.68

Table 3 (continued)

	Properties of coating film			
	60° gloss (%)	Hue		
		L* value (-)	a* value (-)	b* value (-)
Our invention	70-110	-	-	-
Experiment 2	69	34.93	8.16	-13.68

Table 3 (continued)

	Properties of coating film	
	Light resistance ( $\Delta E^*$ value) (-)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Our invention	Not more than 5.0	Not more than 0.11
Experiment 2	13.1	0.1106

Table 4

	Properties of resin composition			
	Dispersing condition (-)	Hue		
		L* value (-)	a* value (-)	b* value (-)
Our invention	Not less than 3	-	-	-
Experiment 2	2	36.13	7.68	-13.71

Table 4 (continued)

	Properties of resin composition	
	Light resistance (ΔE* value) (-)	Transparency (linear absorption) (μm <sup>-1</sup> )
Our invention	Not more than 5.0	Not more than 0.10
Experiment 2	13.7	0.1214

Remarks

As seen from the above Tables, the tinting strength and light resistance ( $\Delta E^*$  value) of the blue silica particles obtained in Experiment 2 (Example VII of U.S. Patent No. 5,378,574) are 108% and 12.1, respectively, which are out of the range of the present invention. As a result, the coating film and resin composition produced by using the blue silica particles obtained in Experiment 2 (Example VII of U.S. Patent No. 5,378,574) are inferior in storage stability ( $\Delta E^*$  value), 60° gloss, light resistance ( $\Delta E^*$  value) and transparency to those of the present invention.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: January 28, 2005

Kazuyuki Hayashi  
Kazuyuki HAYASHI